

Seasonal composition of PM_{2.5} and Performance of the Federal Reference Method in Pittsburgh

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Summary

This paper describes results from the Pittsburgh Air Quality Study (PAQS), a large-scale ambient air quality study focused on particulate matter in the Pittsburgh and Upper Ohio River Valley regions. The PAQS study is a collaborative project involving 20 research groups. Ambient measurements are made at a central supersite located in an urban neighborhood within Pittsburgh, and satellite sites both within the city of Pittsburgh and the surrounding region. A wide array of standard and advance aerosol instrumentation is deployed at the central site including integrated samplers, semi continuous instruments, and single particle instruments.

The data indicate a strong seasonal variation in both PM_{2.5} levels and composition within Pittsburgh. During the summer (July and August) of 2001 the average PM_{2.5} mass concentration in Pittsburgh was 24 µg/m³ with the major components being sulfate (40% of total mass) and organic material (24% of total mass). The average PM_{2.5} level in the fall (September, October and November) of 2001 was 15 µg/m³ with the major components being sulfate (35% of total mass) and organic material (35% of total mass). The average PM_{2.5} level during the first part of the winter (December and half of January) of 2001 was 10 µg/m³ with the major components being sulfate (27% of total mass) and organic material (36% of total mass), and nitrate (19% of total mass). The higher levels of PM_{2.5} in the summer are primarily due to elevated formation of secondary organic aerosol and higher conversion rates of sulfur dioxide to sulfate. The appearance of significant nitrate levels during the winter is due to a combination of lower temperatures and lower sulfate levels.

The results from the PAQS are used to evaluate the performance of the Federal Reference Method (FRM) for ambient concentrations of particulate matter (PM) with an aerodynamic diameter of 2.5 micrometers or less (PM_{2.5}). In July of 1997, the U.S. Environmental Protection Agency revised the National Ambient Air Quality Standards to include regulatory standards for PM_{2.5}. The new EPA standard defines PM_{2.5} as the mass measured by the FRM.

To evaluate the performance of the FRM, daily ambient air samples were taken at Pittsburgh, Pennsylvania using the method during the summer of 2001. These measurements are compared to the sum of chemical components of PM_{2.5} aerosol sampled at the same location during the same period. Monthly average PM_{2.5} concentrations for the months of July and August were 21 and 28 µg/m³. During this two-month period, the sum of the chemical components of the aerosol measured agreed to within 15% of the mass measured by the FRM. However, comparisons on a daily and hourly basis revealed discrepancies of up to a factor of two between the FRM-measured mass and the sum of the aerosol chemical components. On low PM_{2.5} concentration days, the FRM appeared to underestimate the PM_{2.5}

mass (sum of components greater than FRM mass), while on high concentration days the FRM appeared to overestimate the mass (sum of components less than FRM mass). A graph of PM_{2.5} mass vs. the ratio of PM_{2.5} mass to the sum of aerosol chemical components for July and August illustrates this trend, showing the ratio increasing with increasing PM_{2.5} mass, and the ratio below one for several days, all of which had PM_{2.5} concentrations less than 20 µg/m³.

Closer examination of the data reveals several factors that may contribute to the discrepancy between the FRM measurements and the sum of the chemical composition. For example, the FRM appears to overestimate PM_{2.5} mass on days when the atmosphere is acidic. Under these conditions the sulfate in the aerosol will occur as bisulfate, which will likely cause the aerosol to retain significant water even at the low relative humidity conditions that FRM samples are conditioned in for gravimetric analysis. The data also suggest that the FRM may underestimate mass on days with higher organic levels. We are developing a theoretical model to explain the variation between the observed differences between measured FRM mass and the sum of the components.

Measurements have continued since the summer, allowing for an evaluation of the observed trends in cooler temperatures. On an absolute basis, the discrepancy between FRM-measured PM_{2.5} and the sum of the chemical components of the aerosol appears to have steadily declined through the fall and winter, with the discrepancy apparently disappearing in December on a monthly average basis. The period of greatest discrepancy occurred during from the end of July through the first week of August.